FUNCTIONALIZED SORBENT FOR CHEMICAL SEPARATIONS AND SEQUENTIAL FORMING PROCESS

FIELD OF THE INVENTION

The present invention relates generally to sorbent materials and methods for selective capture and retention of target species. More particularly, the invention relates to a porous sorbent and process for chemical separations and retention of preselected gases.

BACKGROUND OF THE INVENTION

Selective capture and retention of unwanted gases, e.g., in flue gas streams, are of high interest. Various methods are known for sorption of gases including, e.g., use of liquids such as monoethanol amine (MEA). However, liquid amines can have volatile emissions, corrode infrastructure, quickly reach saturation, suffer from slow capture kinetics, and can degrade over time, losing capacity. Fluid methods thus have serious limitations for long-term chemical sorption and retention of unwanted gases. Accordingly, new solid phase sorption materials and methods are needed that are stable, exhibit fast sorption kinetics, provide long-term retention of unwanted gases, and are capable of being regenerated, providing for long service lifetimes. Additional advantages and novel features of the present invention will be set forth as follows and will be readily apparent from the descriptions and demonstrations set forth herein. Accordingly, the following descriptions of the present invention should be seen as illustrative of the invention and not as limiting in any way.

SUMMARY OF THE INVENTION

The invention in one aspect is a sequentially functionalized, solid-state sorbent for chemical sorption that provides for capture and retention of preselected target analytes. The sorbent includes: a porous support (substrate) of a preselected porous material that includes pores of a preselected size, pore volume, and surface area. The porous support is composed of a preselected material including, but not limited to, e.g., metals, transition metals, main group metalloids, metal oxides, ceramic oxides, oxide coated materials, metal silicates, including combinations of these porous materials. Metals include, e.g., aluminum (Al), and tin (Sn). Transition metals include, but are not limited to, e.g., titanium (Ti), zirconium (Zr), zinc (Zn), iron (Fe), nickel (Ni), copper (Cu), including combinations of these metals. Main group metalloids include, but are not limited to, e.g., Si, Ge, As, Sb, Bi, including combinations of these metalloids. Metal oxides include, but are not limited to, e.g., Al_2O_3, Ga_2O_3, GeO_2, SnO_2, and combinations of these oxides. Ceramic oxides include, but are not limited to, e.g., SiO_2 and TiO_2. The porous support includes pores with a pore size of from about 30 Å to about 500 Å. The porous support further includes a pore volume that is greater than or equal to about 0.5 cc/g. More particularly, the pore volume is in the range from about 1 cc/g to about 3 cc/g, but is not limited thereto. Porous support includes a specific pore surface area greater than or equal to about 150 m^2/g. More particularly, specific pore surface area is in the range from 200 m^2/g to about 1500 m^2/g. Pores of the porous

support are functionalized with a preselected quantity of short-length (e.g., 5-20 Å) amino silanes that are chemically attached to surfaces (e.g., walls) of the pores, and substantially evenly distributed within the pores. In various embodiments, the short-length amino silanes include a terminal amine group. In one embodiment, the terminal amine group includes diethylenetriamine (DETA). In one embodiment, the short-length organic amino silane is 3-diethylenetriamine (DETA)-propyltrimethoxysilane. Short-length organic amino silanes preferably have a molecular weight of less than about 300 g/mol. Pores of the porous support further include a preselected quantity of organic polyfunctional oligomeric amino silanes (e.g., 25-45 Å) that are chemically attached to surfaces within the pores and interspersed between previously attached short-length amino silanes. The polyfunctional oligomeric amino silanes are substantially evenly dispersed across the pore surface within the pore. In one embodiment, the terminal group of the polyfunctional oligomeric amino silanes includes polyethyleneimine (PEI). In various embodiments, the polyfunctional oligomeric amino silanes have a molecular weight of from about 200 g/mol to about 1000 g/mol, but molecular weight is not limited thereto. Pores of the support further include a quantity of other short-length (e.g., 5-20 Å) amino silanes of like or different kind that are interspersed and chemically attached between previously attached short-length amino silanes and previously attached polyfunctional oligomeric amino silanes that serve to backfill open locations across the surface of the pores, forming the fully functionalized sorbent. The short-length organic amino silanes and organic polyfunctional oligomeric amino silanes in combination define a three-dimensional structure of active binding sites that are oriented substantially orthogonal to surfaces of the pores of the support. Crosslinking of silane groups between the short length organic amino silanes and the organic polyfunctional oligomeric amino silanes at the surface serves to maintain the 3-dimensional structure of amino silanes within the pores and further provides thermal stability of the solid-state sorbent. Amine functional groups present on the backbone of the highly functionalized silanes of the sorbent define active binding sites that provide the sorbent with a preselected functional density, selectivity, and capacity for retention of preselected target analytes. Functional density of the sorbent is defined by at least 3 or more amine functional groups per square nanometer of sorbent surface area. The density of active binding sites provide a preselected selectivity and capacity to selectively sorb, bind, capture, and retain preselected target analytes on the porous support of the sequentially functionalized sorbent when contacted by the analytes, including, e.g., gaseous analytes. Gaseous analytes include, but are not limited to, e.g., HCl, SO_2, SO_3, CO_2, and combinations of these gases. In various embodiments, the binding sites of the sorbent can be further modified to include various functional groups including, but not limited to, e.g., thiols, carboxylates, sulfonates, phosphonates, phosphines, heteroaromatic ligands, ammonium salts, phosphonium salts, and combinations of these functional groups to provide selective binding for various target analytes. Heteroaromatic ligands include, but are not limited to, e.g., pyridines; 1,10-phenanthroline; 2,2'-bipyridine; and combinations of these ligands. The sorbent can be functionalized in various organic solvents, in supercritical fluids, or in the vapor phase. The sorbent can be used as a component of a sorption system or device, e.g., for trapping unwanted gases in a flue gas stream. The sorbent can also be used as a component of, e.g., analysis devices and applications, assay devices and applications, chemical separations